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(54) Title: POLYOL FORMULATION

(57) Abstract: Polyol combination comprising (a) 60 to 95 parts by weight of a polyol component having an average nominal functionality of at least 2.1, an average aromaticity in the range of from 5 to 35 wt.% and an average hydroxyl value in the range of from 200 to 700 mg KOH/g; and (b) 5 to 40 parts by weight up to a total of 100 parts by weight of at least one polyethylene glycol having a molecular weight in the range of from 200 to 1000. The polyol component (a) may consist of a blend of at least two polyols, suitably an aromatic polyol and an aliphatic polyol. The polyol combination is suitably used in a formulation which additionally comprises one or more fire retardants other than dimethyl methyl phosphonate, one or more blowing agents, at least one catalyst and usual auxiliaries. Fire-retardant rigid polyurethane foams can be prepared by reacting the polyol combination with a polyisocyanate component in the presence of at least a catalyst, a foam stabilising agent and a blowing agent.

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## DESCRIPTION

## POLYOL FORMULATION

The present invention relates to a polyol combination, to a formulation comprising such polyol combination, to a process for preparing a polyurethane foam using said polyol combination and to shaped articles comprising such a polyurethane foam.

Rigid polyurethane foams are widely used in the building insulation market as well as in appliances where heat insulation is important, for instance in refrigerators. Often the foams are used in a laminate structure: a core of rigid polyurethane foam is covered on two sides with e.g. a metal facing. Rigid foams are also frequently used as the core material in vacuum insulation panels. Such panels usually comprise a core material enclosed in a vacuum container of metal and/or plastic films.

When used as insulating material the rigid polyurethane must meet certain fire-retardancy requirements. To that effect fire retardants are normally added to the foaming formulations. Such fire retardants often contain phosphorus compounds and/or halogen-containing compounds. In rigid polyurethane laminates the fire retardant conventionally used is dimethyl methyl phosphonate (DMMP). This fire retardant is generally considered to be one of the most efficient liquid non-reactive fire retardants available in the marketplace. However, despite its excellent fire retardancy properties, DMMP more and more becomes the subject of criticism. One important reason for this criticism is the fact that DMMP is prone to be emitted when the waste produced in manufacturing the rigid foam laminates is recycled, e.g. into press boards. During such recycling treatment phosphorus compounds originating from DMMP may be emitted, which is undesired from a health and environmental perspective. Simply replacing DMMP by another fire retardant, which is less prone to emission, has so far not been successful.

Accordingly, it is an object of the present invention to provide a formulation for producing rigid polyurethane foams, which is free of DMMP, but which still exhibits very good fire retardant properties while at the same time being easily processable. It is also an object of the present invention to provide a formulation free of DMMP, wherein the content of phosphorus in the alternative fire retardants used is reduced,

while still exhibiting very good fire retardant properties. Furthermore, the rigid polyurethane foam produced from such formulation should not release any toxic compounds when being subjected to a recycling treatment. Furthermore, this rigid polyurethane foam should have excellent mechanical properties in order to give the laminates the necessary mechanical strength and, when used in laminates, should also have a good adhesion to the plastic or metal facings.

It was found that these objectives could be achieved by using a specific aromatic polyol in combination with polyethylene glycol(s). Using this polyol combination together with fire retardants other than DMMP was found to provide polyurethane foams with a reduced phosphorus content and with fire retardancy properties similar to the conventional foams containing DMMP, while also resulting in foams having excellent adhesion, mechanical and processing characteristics.

Accordingly, the present invention relates to a polyol combination comprising

- (a) 60 to 95 parts by weight of a polyol component having an average nominal functionality of at least 2.1, an average aromaticity in the range of from 5 to 35 wt% and an average hydroxyl value in the range of from 200 to 700 mg KOH/g; and
- (b) 5 to 40 parts by weight up to a total of 100 parts by weight of at least one polyethylene glycol having a molecular weight in the range of from 200 to 1000.

Component (a) of the polyol combination is a rigid polyether polyol component which constitutes the largest part of the polyol combination. The term "polyether polyol" as used in this connection refers to polyols comprising poly(alkylene oxide) chains, which polyols are normally obtained by reacting an initiator compound containing two or more active hydrogen atoms, e.g. in the form of hydroxyl or amine groups, with at least one alkylene oxide and optionally other compounds. The term "molecular weight" as used throughout this specification refers to number average molecular weight. The term "aromaticity" as used throughout this specification is defined as the weight percentage of aromatic carbon atoms (i.e. carbon atoms contained in an aromatic ring structure) present in the polyol relative to the total weight of the polyol.

The polyol component (a) is preferably present in an amount of from 70 to 90 parts by weight. It may consist of a blend of two or more polyols, which blend then has to meet the requirements of functionality, hydroxyl value and aromaticity as defined above. The average nominal functionality of polyol component (a) suitably is from 2.5 to 8, more suitably from 2.5 to 6. The average hydroxyl value suitably ranges from 300 to 650 mg KOH/g, more suitably from 350 to 600 mg KOH/g. The average aromaticity of polyol component (a) suitably ranges from 10 to 30 wt%. The average molecular weight of polyol component (a) suitably ranges from 200 to 1500, more suitably from 400 to 1200, whilst most suitably the average molecular weight will not exceed 1000.

As indicated herein before, the polyol component (a) may consist of a blend of at least two polyols, suitably two or three polyols. In a preferred embodiment the polyol component (a) comprises

(a1) an aromatic polyol having an average nominal functionality of at least 2, an aromaticity in the range of from 10 to 40 wt% and a hydroxyl value in the range of from 200 to 700 mg KOH/g; and

(a2) an aliphatic polyol having an average nominal functionality of at least 3, a hydroxyl value in the range of from 200 to 700 mg KOH/g and a molecular weight in the range of from 300 to 1500.

The amounts of components (a1) and (a2) are such that the overall component (a) meets the requirements of average functionality, average aromaticity and average hydroxyl value specified above for component (a). Suitably, component (a1) constitutes from 30 to 80 wt%, more suitably 40 to 75 wt%, of the total of component (a). Component (a2) is then used in an amount adding up to 100 wt%.

Polyol component (a1) suitably has an average nominal functionality of from 2 to 6, preferably between 2 and 4, an aromaticity in the range of from 15 to 35 wt% and a hydroxyl value in the range of from 300 to 650 mg KOH/g, preferably 400 to 600 mg KOH/g. The molecular weight of polyol component (a1) suitably ranges from 200 to 1500, but preferably is at the low end of this range, i.e. from 200 to 500.

Polyol component (a2) suitably has an average nominal functionality of from 3 to 8, preferably 3.5 to 7, a hydroxyl value in the range of from 350 to 675 mg KOH/g,

preferably 450 to 650 mg KOH/g and a molecular weight in the range of from 300 to 1000, preferably 350 to 700.

Both polyol components (a1) and (a2) are polyether polyols and typically are alkylene oxide adducts of initiators, such as sucrose, sorbitol, pentaerythritol, glycerol, diethanolamine, diethylene glycol, bisphenol A and blends of two or more of these.

The alkylene oxides most frequently used are propylene oxide and ethylene oxide.

For the purpose of the present invention polyether polyols based on propylene oxide as the sole alkylene oxide are preferred. The polyols are typically prepared by reacting the initiator or mixture of initiators with one or more alkylene oxides in the

presence of a suitable alkoxylation catalyst. Suitable alkoxylation catalysts are well known and include alkali metal hydroxides as well as amine catalysts. Suitable amine catalysts include alkanolamines like diethanolamine and triethanolamine, tertiary amines like N,N-dimethylcyclohexylamine, and combinations of two or more of these catalysts. Examples of suitable amine catalysts are, for instance, given in EP-A-0 045 544.

Suitable polyethylene glycols to be used as component (b) are those polyethylene glycols having a molecular weight in the range of from 200 to 1000, preferably from 250 to 800, more preferably from 300 to 600. It will be understood that polyethylene glycols contain two hydroxyl groups, which are available to react with alkylene oxide. The polyethylene glycol component (b) may consist of one or more, preferably one or two, polyethylene glycols. If more than one polyethylene glycol is used, they should all meet the above requirement as to molecular weight. Suitable polyethylene glycols are commercially available from several suppliers or can be prepared by methods known in the art.

In a further aspect the present invention relates to a polyol formulation comprising:

- (i) the polyol combination as described herein before;
- (ii) one or more fire retardants other than dimethyl methyl phosphonate;
- (iii) one or more blowing agents;
- (iv) at least one catalyst; and
- (v) usual auxiliaries.

Fire retardants other than dimethyl methyl phosphonate that may be employed as component (ii) are those fire retardants commonly used in manufacturing rigid

polyurethane foams. Such fire retardants include both reactive and non-reactive fire retardants. The term "reactive" as used in this connection refers to reactive towards isocyanate groups. Examples of non-reactive fire retardants include tris chloro isopropyl phosphate (TCPP), diethyl ethyl phosphonate (DEEP) and triethyl phosphate. Reactive fire retardants typically are halogenated polyols, such as the brominated aromatic polyol based on tetrabromo bisphenol A and sold under the name FOX-O-POL VD280s (ex Resina Chemie; FOX-O-POL is a trademark), the halogenated aliphatic polyol based on a brominated diol and epichlorohydrin and sold under the name IXOL PF50 (ex Solvay; IXOL is a trademark) and the brominated aromatic polyol based on tetrabromo phthalate diol and sold under the name PHT-4-diol (ex Great lakes). The fire retardant is typically used in an amount of from 20 to 150 parts by weight (pbw) per 100 pbw of polyol component (a) of the polyol combination, preferably 30 to 100 pbw per 100 pbw of polyol component (a) and more preferably from 40 to 75 pbw per 100 pbw of polyol component (a).

Suitable blowing agents, which can be used as component (iii), are those conventionally applied in rigid polyurethane production and include water, partly halogenated alkanes, aliphatic alkanes and alicyclic alkanes. Fully halogenated hydrocarbons may also be used, but are less preferred due to their ozone depleting effect. Concrete examples of suitable blowing agents then include water, 1-chloro-1,1-difluoroethane, cyclopentane, cyclohexane, n-pentane, isopentane and mixtures of two or more of these. A combination of water on the one hand and n-pentane or cyclopentane on the other hand has been found particularly useful. The amount of blowing agent used may range from 0.1 to 10 pbw, preferably 1 to 5 pbw, per 100 pbw of polyol component (a) of the polyol combination for water and 0.1 to 40 pbw, preferably 5 to 25 pbw, per 100 pbw of polyol component (a) in case of partly halogenated hydrocarbons, aliphatic alkanes and alicyclic alkanes. Furthermore, low boiling blowing agents which give a frothing effect can also be used. Examples of such blowing agents include liquid carbon dioxide, HFC-134a (1,1,1,2-tetrafluoroethane) and HFC-152a (1,1-difluoroethane).

The polyurethane catalyst, that may be employed as component (iv), can be any urethane catalyst known to be suitable in urethane production. Suitable catalysts are those described in e.g. EP-A-0,358,282 and US-A-5,011,908 and include tertiary

amines, salts of carboxylic acids and organometallic catalysts. Examples of suitable tertiary amines are triethylene diamine, N,N-dimethyl cyclohexyl amine, N-methyl morpholine, diethyl ethanol amine, diethanol amine, dimethyl benzyl amine and dimethyl cyclohexyl amine. Suitable organometallic catalysts include stannous octoate, stannous oleate, stannous acetate, stannous laureate, lead octoate, nickel naphthenate and dibutyltin dichloride. Further examples of organometallic catalysts are described in US-A-2,846,408. Of course, mixtures of two or more of the aforementioned catalysts may also be used. Suitable polyisocyanurate catalysts or trimerisation catalysts are also well known in the art and include sodium acetate, potassium octoate or potassium acetate, e.g. dissolved in diethylene glycol, and strong basic materials, such as quaternary ammonium salts and tris(dimethylaminopropyl) triazine. The amounts of polyurethane catalyst will usually be in the range of from 0.01 to 8.0 parts by weight (pbw), more suitably 0.1 to 5.0 pbw, per 100 pbw of polyol component (a) of the polyol combination.

The auxiliaries, which form component (v), are the usual components and may include foam stabilisers, colouring agents and fillers. The foam stabiliser (or surfactant) used may be any polyurethane foam stabiliser useful in the production of rigid polyurethane foams. Organosilicone or organopolysiloxane surfactants are most conventionally applied as foam stabilisers in polyurethane production. A large variety of such surfactants is commercially available. Usually, such foam stabiliser is used in an amount of up to 3 pbw, per 100 pbw of polyol component (a).

In a still further aspect the present invention relates to a process for preparing a fire-retardant rigid polyurethane foam, which process comprises reacting a polyol combination as described herein before with a polyisocyanate component in the presence of at least a catalyst, a foam stabilising agent and a blowing agent.

The polyisocyanate component may be any polyisocyanate or combination of polyisocyanates known to be suitable for preparing rigid polyurethane foams. Suitably, aromatic polyisocyanates are used and any di-, tri-, tetra- and higher functional aromatic polyisocyanate may be used. In EP-A-0,778,302, for instance, a list with suitable polyisocyanates is given. Preferred polyisocyanates are 2,4- and 2,6-toluene diisocyanate as well as mixtures thereof; 4,4'-diphenylmethane diisocyanate

(MDI); polymethylene polyphenylene polyisocyanate and polymeric MDI, a mixture of polyisocyanates with MDI as the main component.

The quantity of polyisocyanate component to be used should suitably be such that the isocyanate index has a value between 50 and 160, more suitably between 80 and 150 and most suitably between 100 and 145. However, isocyanate indices outside these ranges may also be used. As is well known in the art, the isocyanate index is defined as the 100 times the equivalence ratio of isocyanate groups to active hydrogen atoms present in the polyol combination and water.

The catalyst, foam stabilising agent and blowing agent(s) and the amounts in which they are used in the process of the present invention are the same as those described above in relation to the formulation. However, for the purpose of the present invention it has been found particularly useful to use water and/or at least one alkane, more preferably water and n-pentane, as blowing agent(s).

The present invention also extends to shaped articles comprising a fire-retardant rigid polyurethane foam obtained by the process described above. Such shaped article suitably is a laminate consisting of two metal facings with the fire-retardant rigid polyurethane foam therein between.

The invention is further illustrated by the following examples without restricting the scope of the invention to these particular embodiments.

The ingredients used in the Examples are:

Polyol A: an aromatic, propylene oxide based polyol having an OH value of 510 mg KOH/g, a molecular weight of about 265, a functionality of 2.4 and an aromaticity of 31 wt%.

Polyol B: an aromatic, propylene oxide-based rigid polyol having an OH value of 520 mg KOH/g, a molecular weight of 325, a functionality of 3.0 and an aromaticity of 16 wt%.

Polyol C: an aliphatic, propylene oxide-based rigid polyol having an OH value of 575 mg KOH/g, a molecular weight of 390 and a functionality of 4.0.



PS3152: STEPANPOL PS3152: a polyester polyol ex Stepan based on phthalic anhydride and diethylene glycol having an OH value of 315 mg KOH/g and a functionality of 2.0 (STEPANPOL is a trademark).

5 PEG400: Polyethylene glycol having a molecular weight of 400.

CARADATE 30: polymeric MDI ex Shell (CARADATE is a trade mark).

PHT-4-diol: a brominated aromatic polyol based on tetrabromo phthalate diol ex Great lakes.

10 PF50: IXOL PF50, a halogenated aliphatic polyol based on a brominated diol and epichlorohydrin ex Solvay (IXOL is a trademark).

T CPP: tris chloro isopropyl phosphate.

DEEP: diethyl ethyl phosphonate.

DMMP: dimethyl methyl phosphonate.

15 B8455: TEGOSTAB B8455, a silicone surfactant ex Goldschmidt (TEGOSTAB is a trade mark).

B8404: TEGOSTAB B8404, a silicone surfactant ex Goldschmidt.

JEFFCAT TR: catalyst blend ex Huntsman (JEFFCAT is a trademark).

DMCHA: N,N-dimethylcyclohexylamine.

20 Examples 1 and 2

Polyol formulations having a composition as indicated in Table 1 were prepared by mixing the ingredients in the relative amounts indicated while stirring, using an explosion proof stirrer at a speed of 3000 rpm. Subsequently, the polyisocyanate was added to the formulations over a period of five seconds and the resulting foaming mixtures were stirred for another five seconds before they were poured into open polyethylene bags, where the foaming occurred.

25 Fire retardancy properties of the resulting foams were measured according to the DIN4102 B2 small scale fire test: a flame height of 15.0 cm or less means that the foam has passed the test. For this test samples having a thickness of 2 cm were used.

30 Free rise density was determined on a cube of 10x10x10 cm<sup>3</sup>, cut from the centre of the bag foam, according to ISO 845. Compressive strength in the rise direction of the

foam was determined on samples of 5x5x2.5 cm<sup>3</sup> according to the standard test BS4370/1.

The results are indicated in Table 1.

5      Comparative Examples 1-3

Example 1 was repeated except that different formulations were used: a standard DMMP-containing formulation (Comparative Example 1) and two formulations not containing a polyethylene glycol, but instead a higher amount of fire retardant (Comparative Examples 2 and 3).

10      The formulations and the foam properties are indicated in Table 1.

From Table 1 it can be seen that the DMMP-free foams based on a polyol combination in accordance with the present invention exhibit a fire retardancy which is comparable to a conventional DMMP-containing foam and to DMMP-free foams based on polyol combinations free of polyethylene glycol. Moreover, the foams of the

15      present invention contain less phosphorus and have excellent mechanical properties.

Table 1 Formulations

	Ex 1	Ex 2	C-Ex 1	C-Ex 2	C-Ex 3
Polyol A (pbw)	45			45	
Polyol B (pbw)		45	48		45
Polyol C (pbw)	20	20	16	20	20
PEG400 (pbw)	15	15			
PS3152 (pbw)			15		
PHT-4-diol (pbw)	25	25		35	35
PF50 (pbw)			20		
DMMP (pbw)			15		
DEEP (pbw)	10	10		15	15
TCPP (pbw)	20	20	15	20	20
B8455 (pbw)	1.5	1.5		1.5	1.5
B8404 (pbw)			1.5		
JEFFCAT TR (pbw)	0.6	0.6	1.0	0.6	0.6
DMCHA (pbw)	0.6	0.6	1.0	0.6	0.6
Water (pbw)	2.5	2.5	2.4	2.45	2.4
n-pentane (pbw)	10.5	10.5	9.4	10.2	10.5
Caradate 30 (pbw)	179	181	215	172	174
Isocyanate index	125	125	143	125	125
Foam properties					
Flame height (cm)	12.5	14.0	12.7	12.5	13.5
Density (kg/m <sup>3</sup> )	32.0	30.3	30.2	31.9	30.7
Compr. Strength (kPa)	214.1	185.7	190	190.0	175.1
Phosphorus (wt%)	1.2	1.2	1.5	1.5	1.5

## CLAIMS

1. Polyol combination comprising (a) 60 to 95 parts by weight of a polyol component having an average nominal functionality of at least 2.1, an average aromaticity in the range of from 5 to 35 wt% and an average hydroxyl value in the range of from 200 to 700 mg KOH/g; and (b) 5 to 40 parts by weight up to a total of 100 parts by weight of at least one polyethylene glycol having a molecular weight in the range of from 200 to 1000.
2. Polyol combination as claimed in claim 1 comprising 70 to 90 parts by weight of component (a) and 10 to 30 parts by weight of component (b).
3. Polyol combination as claimed in claim 1 or 2, wherein the polyol component (a) has an average nominal functionality of 2.5 to 8.
4. Polyol combination as claimed in any one of the preceding claims, wherein the polyol component (a) has an average hydroxyl value of 300 to 650 mg KOH/g.
5. Polyol combination as claimed in any one of the preceding claims, wherein polyol component (a) consists of a blend of at least two polyols.
6. Polyol combination as claimed in claim 5, wherein the polyol component (a) comprises (a1) an aromatic polyol having an average nominal functionality of at least 2, an average aromaticity in the range of from 10 to 40 wt% and an average hydroxyl value in the range of from 200 to 700 mg KOH/g; and (a2) an aliphatic polyol having an average nominal functionality of at least 3, an average hydroxyl value in the range of from 200 to 700 mg KOH/g and a molecular weight in the range of from 300 to 1500.
7. Polyol combination as claimed in any one of the preceding claims, wherein component (b) consists of one polyethylene glycol having a molecular weight in the range of from 250 to 800.
8. Polyol formulation comprising (i) the polyol combination as claimed in any one of claims 1 to 7; (ii) one or more fire retardants other than dimethyl methyl phosphonate; (iii) one or more blowing agents; (iv) at least one catalyst; and optionally (v) usual auxiliaries.
9. Process for preparing a fire-retardant rigid polyurethane foam, which process comprises reacting a polyol combination as claimed in any one of claims 1 to 7

with a polyisocyanate component in the presence of at least a catalyst, a foam stabilising agent and a blowing agent.

10. Process as claimed in claim 9, wherein water and/or at least one alkane is used as blowing agent.

5 11. Shaped article comprising a fire-retardant rigid polyurethane foam obtained by a process as claimed in claim 9 or 10.

12. Shaped article as claimed in claim 11, which is a laminate consisting of two metal facings with the fire-retardant rigid polyurethane foam therein between.

## INTERNATIONAL SEARCH REPORT

International Application No

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## A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 44 39 994 A (ALCARE) 8 June 1995 (1995-06-08) page 4, line 11 -page 5, line 10; examples ---	1
A	US 4 427 797 A (SMITH) 24 January 1984 (1984-01-24) column 4, line 56 -column 5, line 11; example 2 ---	1
A	EP 0 778 302 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ) 11 June 1997 (1997-06-11) cited in the application page 3, line 3 -page 5, line 32; claims; examples ----- -/--	1

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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